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NATURAL POZZOLANS

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INTRODUCTION

The recent volcanic eruption in Columbia in which more than 20,000 human lives were lost shows that volcanic eruptions can be highly destructive. In May 1980, the eruption of Mount St. Helens in the Oregon State left behind a 200 square miles of wasteland containing buried forests, streams, and lakes. It is reported that about 400 million tons of volcanic ash and rock were hurled into the environment and the ash clouds covered the skies in the northwest United States for several days.

In 79 A.D., a similar volcanic eruption at Mount Visuvius in Italy engulfed Herculaneum, Pompeii and many other towns along the Bay of Naples with ash, pumice, and mud that caused large-scale death and destruction. In 1500 B.C., a powerful volcanic eruption in the Santorini Island (Greece) produced so much lava and ash that high waves of the order of 80 to 100 meters were generated in the Agean sea which resulted in the total destruction of a well developed civilization, namely the Minoans.

However, not all the consequences from volcanic eruptions are bad. Under hydrothermal conditions, the volcanic ash is transformed into zeolitic tuff and, eventually, to clay minerals that constitute agricultural soils. Also, long ago it was discovered that volcanic ash or pulverized tuff, when mixed with lime, produced calcium silicate hydrates that not only are cementitious but also hydraulic (i.e., water resistant). Ancient structures in Greece and Italy provide sufficient evidence of the durability of lime-pozzolan cements.

For the construction of aqueducts, bridges, buildings, and waterfront walls, the Romans widely used a zeolitic tuff, found in the foothills of Mount Visuvius at Pozzuoli. Thus, this material was popularly known as pozzolana. When similar volcanic materials that reacted with lime were discovered in Germany, France, Spain, and other parts of the world, the term "pozzolana or

pozzolan" was employed as a general term to designate any material, regardless of its geological origin, which would react with lime to produce a cementitious product. Until the advent of the calcium silicate cements (portland cement) in the 19th century, pozzolan-lime mixtures were the primary cementing materials throughout the world for the construction of masonary and hydraulic structures.

Unlike volcanic glass and zeolitic tuff, the clay minerals do not readily react with lime unless their crystalline structure is destroyed by heat treatment. Thus geological constraint to the prduction of lime-pozzolan cements was removed when it became obvious that pozzolans can be made by heat treatment of non-pozzolanic clays and shales. Diatomaceous earths, consisting of opaline or amorphous hydrated silica, were also found to exhibit excellent pozzolanic characteristic. However, they are generally contaminated with clay and therefore have to be heat treated to enhance the lime-reactivity.

According to ASTM C 618, a pozzolan is defined as a siliceous or siliceous and aluminous material which in itself possesses little or no cementitious value but will in finely divided form and in the presence of moisture chemically react with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties. This definition rules out ordinary quartzite sand to be categorized as a pozzolan, because mixtures of pulverized sand and lime will require hydrothermal treatment to form cementitious products. However, the definition of a pozzolan includes several industrial byproducts, such as fly ash, rice husk ash, and condensed silica fume which can react with lime at ordinary temperature.

Since the advent of portland cement in the 19th century, lime-pozzolan mixtures are seldom used for making structural concrete. This is because portland cement sets and hardens at a considerably faster rate than lime-

pozzolan mixtures. Portland cement consists mainly of tricalcium and dicalcium silicates, which on hydration produce calcium silicate hydrates and calcium hydroxide (hydrated lime). Since calcium hydroxide is not a cementitious material, it can be converted into one if a pozolan is added to the concrete mixture. This can be achieved either by blending the pozzolan with the portland cement or by using the pozzolan as a direct admixture to concrete. Regardless of how a pozzolan is used, the pozzolanic reaction and the benefits associated with it remain the same. The main technical advantages from the use of pozzolans in portland cement concrete include improvement in workability, reduced heat of hydration and risk of thermal cracking, increased water tightness, better durability to sulfate and acidic environments, and enhanced resistance to cracking by alkali-aggregate reaction.

This report contains a description of history of the use of natural pozzolans in the world, classification and composition of natural pozzolans, thermal activation of raw pozzolan, the pozzolanic reaction and its effects, specifications and test methods, and properties of concrete containing natural pozzolans.

HISTORY OF THE USE OF NATURAL POZZOLANS IN THE WORLD

Before the invention of portland cement in 1824, lime-pozzolan mortars and concretes were in use throughout the world. After portland cement became available, the use of lime-pozzolan mixtures for cementitious purposes declined gradually due to their relatively slow setting and hardening characteristics. However, for economic reason and to achieve certain technical benefits, mixtures of portland cement and pozzolans are still

commonly used in concrete construction. The history and the use of natural pozzolans in some countries of the world are described next.

According to Lea (1) there is evidence that the Minoan structures of Crete Island, built about 1500-2000 B.C., contained crushed potsherds (i.e., calcined clay) in lime mortar. The use of lime-natural pozzolan concrete has been discovered in a 600-700 B.C. old lining for a water tank in the ancient Greek city of Camiros, Rhodes Island. According to Effstathiadis (2), it seems that volcanic ash from Santorini, called Santorin Earth, was employed for making the concrete which is still in a strong and durable condition. In a relatively recent period, Santorin Earth has been used in concrete for the Suez canal lining. As a pozzolanic material it still enjoys high reputation on the Mediterranean. For reasons of economy and energy conservation, all portland cement produced in Greece routinely contains 10 percent Santorin Earth.

It is well known now that the Romans widely practiced the art and science of building construction developed by the Greeks. Volcanic materials similar in properties to Santorin Earth were discovered in Puzzouli at the Bay of Naples and in Segni, which is in the Latium District near Rome. According to Lea (1), the Romans may also have used pozzolans from crushed tiles before they discovered the deposits in Puzzouli and Segni. They seem to have carried their knowledge of preparing moisture-resistant mortar from lime-pozzolan mixtures to all parts of their Empire including Germany, France, and England. The Rheinisch trass in Germany, a volcanic tuff, was probably discovered during the Roman period. In addition to concrete lining for aqueducts, as decribed by Malinowski (3), lime-pozzolan concrete was widely used by the Romans for the construction of cisterns, water-front walls, and brickwork in buildings.

One of the most famous Roman buildings is the Pantheon, the 20-feet thick walls of which are made of lime-pozzolan cement mortar thinly faced with brick while the large dome (142-feet span) is cast solid in concrete containing pumicite pozzolan. Since many of the Roman structures are in excellent condition even today, they serve as a testimony to the long term durability of well made lime-pozzolan cement products. It may be noted that during the 9 to 12th century period, the art of making lime of a proper quality was lost in Europe (1), however after the 15th century it was grdually reestablished. The lime-pozzolan concrete, such as the one used in the Palace of Versailles, is of excellent quality.

According to Collepardi (4), a considerable amount of natural pozzolan is still used in Italy. In 1984, the total cement production of Italy was 36 million tonnes and about 40 percent of the cement was of the portland-pozzolan type containilng 25% pozzolan. Therefore, 3.5 million tonnes of pozzolans are being used every year for making blended portland cement. Further, according to Collepardi, about 85% or 3 million tonnes of the pozzolan thus used comes from natural sources, the rest being fly ash.

The German trass mentioned above, is found in the neighborhood of Koblenz on the Rhein river and in Bavaria. Trass deposits are also found in Romania and the Soviet Union. According to Lea (1), the Rheinisch trass has been known for about 2000 years because mortars containing the trass have been found in old Roman buildings along the Rhein. Since about the end of the 17th century, German trass has been widely used first in lime-pozzolan cements and later as an additive to portland cement.

In the Federal Republic of Germany trass has been standardized in DIN 51043, which differentiates between the Rheinischer Trass and the Bayerischer Trass. The latter, according to Locher (5) was originally a sedimentary rock but was transformed to suevite by the impact of a meteriorite. Another

zeolitic rock called phonolite, which is found in southwest Germany near Freiburg, is used as a pozzolan. However, it becomes sufficiently reactive to lime only after heat treatment at 300 to 600°C (6). The amount of pozzolan cements produced in Germany today is not large. Locher estimates that in 1984 about 40,000 tonnes of trass and 10,000 tonnes of phonolite were used for making blended portland cements.

In the United States, according to Price (7), the first large use of the portland-pozzolan cement, composed of equal parts by volume of a portland cement and a deeply altered rhyolite tuff, occurred in Los Angeles aqueduct, where about 1×10^5 tonnes of the cement were employed during the years 1910 to 1912. Meissner (8) reported that the Santa Cruz Cement Company at Davenport, California produced a portland-pozzolan cement containing calcined Monterey shale as a pozzolanic ingredient. In 1930's, the cement was used by the California Division of Highways in several structures including the Golden Gate Bridge and the San Francisco-Oakland Bay Bridge. The main reasons for the use of this cement was its proven resistance to sulfate water together with the favorable heat generation characteristics in massive blocks of concrete. In 1935, a portland-pozzolan cement was used in the construction of Bonneville Dam which is located on Columbia river between Oregon and Washington States.

The first application of a natural pozzolan as a mineral admixture was in 1920's when a raw rhyolite pumicite was used in one of the abutments of Big Dalton Dam by the Los Angeles Flood Control District, as a 20 percent by weight replacement of the portland cement. In 1930's, this organization made similar use of this material in several other structures.

In 1933, the U.S. Bureau of Reclamation undertook an intensive study on utilization of natural pozzolans for the purpose of controlling the heat of hydration in concrete for large dams. According to Mielenz (9), as a result

of the Bureau's investigation rhyolitic pumicite was used as an admixture in concretes for the construction of Friant Dam on the San Joaquin River and Altus Dam in Oklahoma. Later in 1947, a calcined siliceous pozzolan was used as a mineral admixture in Davis Dam (Nevada-Arizona), primarily to control alkali-aggregate reaction. Other applications of natural pozzolans in the western United States included Glenn Anne, Cachuma, Trenton, Monticello, Glenn Canyon, Flamingo George, Falcon, Priest Rapids, Wanapum, and John Day dams. Milenz further reports that materials suitable for use as pozzolans either by calcination and grinding or by grinding alone are wide-spread in the United States, but tested sources are mainly west of the Mississippi River. In many cases, pozzolans of natural origin were produced for a specific project but the operation was abandoned after completion of the work. Portland-pozzolan cements composed of natural pozzolans are no longer being produced in the United States.

Among the countries where blended portland cements containing natural pozzolan continue to play an importnt role in the construction industry are China and Mexico. According to Wu (10), zeolitic tuff and calcined coal shale are the main sources of natural pozzolan in China. It is estimated that in 1984 China produced 90 million tonnes of cement containing over 5 million tonnes of zeolitic rock and 6 million tonnes of calcined coal-shale. Wu believes that, in 1990's due to the increasing demand for cement in China, the amount of natural pozzolan used for cement production is bound to increase substantially.

Similarly, in Mexico about one-third of the total cement consumed every year is a blended portland cement containing natural pozzolan. Ten years ago the annual cement consumption of Mexico was 10.6 million tonnes and about 13 percent of the cement was of the blended variety containing a natural

pozzolan. In 1984, Mexico consumed 18.3 million tonnes of cement including 6.3 million tons (34.2 percent) of blended portland cement containing natural pozzolans. According to Poo (11) several forms of natural pozzolans are found in different regions of Mexico, such as pumicite in Jalisco, diatomite in Baja California, and zeolitic tuff in Guanajuato.

CLASSIFICATION AND COMPOSITION

It is not always easy to classify a natural pozzolan because natural materials seldom contain only one lime-reactive constituent and their composition and properties vary over a wide range. However, based on the principal lime-reactive constituent present, the natural pozzolans can be classified into four categories (i.e., unaltered volcanic glass, volcanic tuff, calcined clay or shale, and raw or calcined opaline silica. Typical oxide analyse and mineralogical description of some of the well known pozzolans in the world, which are discussed next, are given in Tables 1 and 2, respectively.

Volcanic Glass

Natural pozzolans that derive their lime-reactivity mainly from unaltered aluminosilicate glass belong to this category. Pozzolans from santorin (Greece), Bacoli (Italy), Shirasu (Japan), Jalisco (Mexico), and rhyolitic pumicites found in several Western States of the U.S. are examples of pozzolans that are composed of volcanic glass.

Mineralogical analyses show that small amounts of non-reactive crystalline minerals are invariably present in the natural pozzolans. In Fig. 1 X-ray diffractogram of a typical sample of Santorin earth is shown (11). Typically, the material consists of about 80 percent volcanic glass (pumice and obsidian)

and 20 percent quartz and feldspar (anorthite and labradorite). Similarly, according to Costa and Massazza (13) the vitreous or glassy matrix of the Bacoli pozzolan contains inclusion of several crystalline minerals, such as leucite, feldspar, and augite. Takemoto and Uchikwa (14) reported the mineralogical analysis of a specimen of the Shirasu pozzolan from Japan, which contained 95 percent glass with quartz and feldspar as the principal crystalline impurities.

According to a personal communication from Poo (11), the Jalisco pozzolan of Mexico, typically, consists c about 90 percent pumice glass and 10 percent sanidine feldspar. Of the 70 materials from the Western U.S. investigated for pozzolanic activity by Mielenz et al (15), 12 owed their pozzolanic activity almost exclusively to rhyolitic glass. In addition, 10 materials owed a significant portion of their activity to volcanic glass. According to the authors, basaltic glass appears to be inferior as a pozzolan than the acidic glasses, such as rhyolite and andesite.

The typically microporous texture of the volcanic glass is evident from the scanning electron micrograph of a specimen of Santorin Earth, shown in Fig. 2. In addition to the disordered or glassy structure, the high specific surface is responsible for the chemical reactivity of the material. Surface area analyses of several samples of Santorin Earth by the BET nitrogen adsorption technique gave values in the range 3800 to 15500 m^2/kg (12).

Volcanic Tuff

The alteration of volcanic glass under hydrotherm conditions leads to the formation of zeolite minerals which have variable chemical composition of the type, $(R_2Ca)O \cdot A\ell_2O_3 \cdot 4SiO_2 \cdot xH_2O$ where R stands for Na or K. Volcanic tuffs are the product of hydrothermal action on valcanic ash, and are characterized by a

hard and compact texture. Unlike volcanic glass, the reactivity of zeolitic minerals with lime is attributed to a base-exchange process between calcium in lime and the alkalies in the volcanic tuff. In general, natural pozzolans that derive their lime-reactivity from base exchange are categorized as volcanic tuffs.

According to Lea (1), the zeolitic compounds commonly found in altered volcanic glass are analcite, chabazite, herschellite, and phillipsite. Analcite corresponds to the chemical composition, $Na_2O \cdot Al_2O_3 \cdot 4SiO_2 \cdot 2H_2O$, chabazite to $(R_2Ca)O \cdot Al_2O_3 \cdot 4SiO_2 \cdot 6H_2O$, herschellite to a corresponding compound richer in alkalies, and phillipsite to a potassium-rich compound. The Roman pozzolans from the Calleferro region contain herschellite, chabazite, and phillipsite, whereas the Napolitan tuffs contain herschellite, analcite, and glauconite ($K_2O \cdot Fe_2O_3 \cdot 4SiO_2 \cdot xH_2O$).

The mineralogical analysis of the German trass as reported by Schweite et al (16), shows that they contain 10-15% quartz, 15-20% feldspar, small amounts of kaolinite and montmorillonite, and about 50 percent of glassy matrix that has undergone alternation to zeolitic minerals. From Freiburg in Southwestern Germany comes another pozzolan, called phonolite, which derives its hydraulic reactivity from zeolites belonging to natrolite group. According to Kassautzki (6), a marked increase in the hydraulic reactivity of phonolite is obtained after heat treatment at 300 to 600°C.

In the United States, many of the 70 specimens investigated for pozzolanic activity by Mielenz et al (15) contained altered rhyolitic tuff. Two Californian pozzolans, from Monolith and Coachella owed their pozzolanic activity essentially to the altered rhyollic tuff containing no volcanic glass but including clinoptilolite (silica-rich heulandite). The Mexican pozzolan from the Guanajuata region is a zeolitic tuff containing clilnoptilolite, quartz, and feldspar (11).

Calcined Clay or Shales

Volcanic glass and tuff do not require heat treatment to enhance the lime reactivity, however, natural materials consisting essentially of clay minerals require heat treatment. When heated to temperatures of the order of 600 to 1000°C, usually in an oil, gas, or coal-fired rotary kiln, the clay minerals decompose to form an amorphous or a disordered aluminosilicate structure that reacts readily with lime at ordinary temperature. Surkhi in India and Hombra in Egypt, produced by pulverizing baked-clay tile or brick, also belong to this category. However, any baked-clay product may not produce a good pozzolan. Obviously the heat treatment of a clay or shale which contains large amounts of highly crystalline minerals, such as quartz and feldspar, would not produce a material possessing adequate reactivity with lime.

According to Mielenz (9) natural materials that include substantial proportions of kaolinite-type or montmorillonite-type clay minerals or combinations thereof require calcination at temperatures in the range 540 to 980°C to induce optimum pozzolanic activity. However, montmorillonite clay in which a large amount of exchangeable sodium cation is present should be avoided, especially if the aggregates proposed for use in the concrete are susceptible to a deleterious degree of alkali-aggregate reaction. Illitic clays and shales containing substantial proportions of Vermiculite, chlorite and mica are generally not suitable sources of pozzolans when the calcination temperature is below 1100°C.

Opaline Silica

Opaline materials including diatomaceous earths and silica gel belong to this category. Diatomaceous earths are of organogen origin. They contain

hydrous, non-crystalline silica composed of skeletal shells from the cell walls of many varieties of aquatic algae of microscopic size. Opal is generally formed as a hydrated silica gel in sediments when the soluble oxides have been leached away from the minerals.

Large deposits of diatomaceous earth are found in Algiers, Canada, Denmark, Germany, India, Mexico, and the United States. Nine of the 70 materials tested for the pozzolanic activity by Mielenz et al (15) were diatomites from the states of California and Washington, two materials owed their pozzolanic activity wholly to opal (gelatinous or non-crystalline silica) mixed with beta cristobalite, and many other materials owed a significant proportion of their activity to opaline chert, sandstone, or shale.

Opaline materials are very reactive to lime but their high specific surface results in unusually large water requirement in concrete mixtures, which is harmful to strength and durability. Furthermore, they generally contain large amounts of clay minerals. To enhance the use of such materials as pozzolans, it is often necessary to heat treat them.

Gaize is a soft and highly siliceous sedimentary rock containing some clay, which is found in the Ardennes and Meuse valleys in France. The material contains silica in gelatinous condition and can be used in the raw state as a pozzolan, but it is more suitable when calcined at a temperature of about 900°C. Lea (1), reported that a portland-pozzolan cement containing burnt gaize was used at Boulogne, Havre, St. Malo, Dieppe, and other French ports for making concrete sea-structures.

Moler, a Danish pozzolan, is a diatomite containing large amount of clay. According to Lea, a moler cement containing 75 percent portland cement and 25 percent moler has been manufactured in Denmark and used for concrete

structures in seawater. Initially, the raw moler was used; later burnt moler was found to be superior and was used instead of the raw product.

Airox, a proprietary product produced in Santa Maria, California, by calcination (and subsequent grinding) of an oil-impregnated diatomaceous shale, has a surface area of the order of 12000 m^2/kg by BET nitrogen adsorption. A sample of this material showed excellent pozzolanic activity as required by the ASTM C 618 Specification, i.e., 9.5 MPa (1370 psi) compressive strength in 7 days in the lime-pozzolan mortar and 4540 psi compressive strength in 28 days in the portland cement-pozzolan mortar (17).

THERMAL ACTIVATION OF RAW POZZOLAN

Many natural pozzolans can be used in the as-mined or raw state after removal of coarse (> 75 μm) particles. Moist materials may have to be dried and pulverized before use. Zeolitic rock has to be crushed and ground to particle size mostly below 75 μm. Calcination of zeolitic tuff or opaline shale may not enhance the pozzolanic activity unless a significant proportion of clay minerals are present. However, clays and shales, or pozzolanic materials containing substantial amount of clay or shale must be thermally activated (i.e., heat treated) in order to develop an acceptable level of pozzolanic activity. The results of a comprehensive study by Mielenz et al (15) on the effect of thermal activation on different types of pozzolans are described next.

Of the 70 materials investigated twelve owed their activity primarily to volcanic glass, with 70-73% of SiO_2 content. The glass type was rhyolitic and its content in the pozzolan ranged from 40 to 100%. In addition to these twelve, ten materials owed a significant portion of their activity to volcanic glass. Through hydorthermal alteration and weathering, the original glass of

most of the volcanic pozzolan had been changed generally to montmorillonite-type clays, or less commonly to kaolinite-type clay or zeolite. Consequently, the response of volcanic glasses to heat treatment depended on an amount of clay minerals present. It was concluded that the physical properties and pozzolanic activity of volcanic glass type pozzolans was only slightly affected by calcination to temperatures as high as 1000°C.

Eleven of the 70 materials investigated by Mielenz et al (15) belonged to the category of hydrous amorphous silica (i.e., diatomites, and opaline cherts and shales). Heat treatment to about 450°C did not cause any change in properties and activity but calcination to 1100°C produced significant changes in behavior. For the material calcined to 750-1000°C, the setting time of the portland cement-calcined pozzolan mixture was significantly reduced and the compressive strength was significantly improved, but this improvement in the pozzolanic behavior was lost at the higher calcination temperatures. It seems that dehydrated amorphous silica structure was more reactive than the hydrous form. Also, partial sintering reduced the surface area of the natural material; thus the lower water requirement of the partially sintered material was responsible for reduction in the setting time and for increase in strength of the portland-pozzolan mixtures. The pozzolanic behavior of opaline materials appeared to be quite sensitive to the temperature of calcination because calcination at 1100°C increased the setting time and decreased the strength probably as a result of over-sintering associated with a substantial loss of activity.

Thirteen of the investigated materials by Mielenz et al (15) contained montmorillonite as the essential ingredient, three had essentially kaolinite, and fifteen contained a mixture of clay minerals including illite and vermeculite. The authors concluded that calcination of clayey materials was essential to develop satisfactory pozzolanic activity, however, the response

to heat treatment varied with the type of clay minerals present. The hydrous aluminum silicates of the kaolinite group lost the water of hydration between 320 to 500°C and thereafter showed significant increase in pozzolanic activity, however above 900°C a reduction in the surface area caused a drop in the activity. At very high temperatures, non-reactive crystalline minerals such as mullite were formed.

The minerals of the montmorillonite group lost most of the water of crystallization between 150° to 510°C; the dehydration was essentially complete by 650°C but the crystal structure was not destroyed until about 870°C. Correspndingly, optimum strength and setting time properties in portland cement-calcined montmorillonite mixtures were obtained for calcination temperatures in the range 650 to 870°C. Illite and vermiculite-type clays were not found to be most promising from the standpoint of strength development. Also, a zeolitic tuff containing 80% clinoptilolite showed some improvement in pozzolanic activity after calcination.

Jun-yuan et al (18) described the results of an investigation on the effect of heat treatment on a zeolitic tuff obtained from near the Nevada Test Site. The material consisted mainly of clinoptilolite and sanidine, with quartz and plagioclase feldspar present as minor phases. The natural tuff was calcined in a muffle furnace to 400°, 600°, 800°C, and 950°C for 2 hours. The compressive strength of 28-day old portland cement mortars both with and without natural or calcined pozzolan (35% cement replacement by volume in the test mortar) were determined. Although the effect of thermal treatment on the strength of tuff-bearing cements was not found to be remarkable, compared to the natural or uncalcined tuff a slight increase in the strength of mortars containing tuff calcined at 400 to 600°C was noticed. Also, it was found that

the reactivity of tuff calcined at 800°C was decreased as a result of reduction in the surface area due to partial sintering.

THE POZZOLANIC REACTION

ASTM C 618 chemical requirements for natural pozzolan prescribe that for use with portland cement concrete the sum of SiO_2, Al_2O_3, and Fe_2O_3 must be at least 70 percent. It is assumed that in a mixture of portland cement with pozzolan and water, when SiO_2, Al_2O_3, and Fe_2O_3 in the pozzolan are present in an amorphous or poorly crystalline structure, these oxides will chemically react with calcium hydroxide (produced by the hydration of calcium silicates in portland cement) at ordinary temperature to form compounds possessing cementitious properties. Except for zeolites, which develop their cementitious property with lime by a base-exchange mechanism as already described, it is the acid-base type reactions between lime and the acidic oxides of a pozzolan that are mostly responsible for technical improvements in concrete containing the pozzolan.

Natural pozzolans generally contain 60 to 85% SiO_2 (Table 1), therefore the main pozzolanic reaction involves the formation of calcium silicate hydrate (C-S-H)* of the type that is formed from the hydration of the principal calcium silicate compound (i.e., C_3S) of portland cement:

(1) $CH + S + aq \longrightarrow C\text{-}S\text{-}H$ (the pozzolanic reaction)

(2) $C_3S + aq \longrightarrow C\text{-}S\text{-}H + CH$ (portland cement hydration).

The pozzolanic reacton is slow, therefore the strength development rate and the heat of hydration associated with this reaction are low; the hydration of

*Cement chemistry notations are used: C = CaO, S = SiO_2, A = Al_2O_3, F = Fe_2O_3, $\bar{S}$ = SO_3, H = H_2O.

C_3S in portland cement is fast, therefore the strength development rate and the heat of hydration associated with it are high. Moreover, it should be noted that the former is a lime-consuming reaction whereas the latter is a lime-producing reaction.

Although the principal pozzolanic reaction is the chemical reaction involving lime and silica, it has been pointed out earlier that cementitious products are also formed as a result of the chemical reactions between lime and alumina or iron oxide. Typically, these products consist of calcium aluminate hydrates or calcium aluminoferrite hydrates. Since portland cement-pozzolan mixtures also contain sulfate (as the interground gypsum in portland cement), calcium sulfoaluminate and sulfoaluminate ferrite hydrates may form instead. In conclusion, the essential difference between the pozzolanic reactions and the reactions involving the hydration of portland cement alone is not in the composition of the hydration products but in the rate at which these are formed. It may be noted that the pozzolanic reactions can be accelerated by temperature, and by the presence of chemical admixtures, such as alkalies and sulfates.

CHEMICAL AND PHYSICAL MANIFESTATIONS OF THE POZZOLANIC REACTION

According to Turriziani (19), at ordinary temperature calcined kaolin and calcium hydroxide react to form gehlenite hydrate (C_2ASH_8) and a calcium silicate hydrate (C-S-H) of variable CaO/SiO_2 ratio which ranges from 0.8 to 1.5. However, Massazza and Costa (20) used several varieties of Italian pozzolans and concluded that the CaO/SiO_2 and H_2O/SiO_2 ratios of the 90-day reaction product were 1.20 to 1.68 and 1.67 to 2.61, respectively, which are in the composition range of C-S-H formed by the hydration of C_3S (the principal compound in portland cement).

When a mixture of portland cement and a pozzolan is hydrated, with the progress of the pozzolanic reaction a gradual decrease of the free calcium hydroxide with time occurs, as illustrated by Fig. 3. For instance, the free calcium hydroxide content in the 1-year old hydrated cement pastes containing 10, 20, or 30 percent Santorin Earth was found to be 13.0, 11.2, and 8.4%, respectively, compared to 16.2% for the reference portland cement paste (12). This shows that in the 30 percent Santorin Earth cement up to 25% of the available calcium hydroxide had been consumed by the pozzolanic reactions. In summary, compared to a well hydrated portland cement paste, the corresponding paste containing a pozzolan will contain less calcium hydroxide and more C-S-H. Additionally, it has been suggested (13) that the CaO/SiO_2 ratio in the C-S-H present in a hydrated portland-pozzolan cement is somewhat lower than the C-S-H typically formed in hydrated portland cements and that it may partly account for the superior chemical resistance of the former.

Recent work by many researchers has confirmed that rather than the chemical manifestation the physical manifestation of the pozzolanic reaction which involves pore refinement of the cement paste is probably more important for the enhancement of chemical durability and mechanical strength. Pore size distribution plots were obtained with mercury intrusion porosimetry on 28-day, 90-day, and 1-year old pastes containing portland-Santorin Earth cements (11). The data from the pore size distribution analysis, arbitrarily divided into pore volumes < 45Å, 45-500Å, 500-1000Å, and > 1000Å, is illustrated in Fig. 4. There is evidence that large pores (viz. > 1000Å or perhaps > 500Å) are associated with lower strength and higher permeability. The data showing the effects of the age of hydration and amount of pozzolan present in the cement paste on a 3-hour water penetration test are given in Table 3. It may be observed that significant reduction in water permeability was obtained for

cements containing 20 or 30 percent pozzolan (age 1-year) when the process of pore refinement, i.e., the conversion of >1000Å pores to smaller pores was essentially complete. A diagrammatic representation of reduction in large capillary pores as a result of the formation of the products of the principal pozzolanic reaction (CH + S → C-S-H) is shown in Fig. 5.

SPECIFICATIONS AND TEST METHODS

According to ASTM C 618, natural pozzolans in raw or calcined state, are designated as Class N Pozzolans. For use as additives to portland cement or as mineral admixtures in portland cement concrete, all pozzolanic materials are required to meet certain chemical and physical requirements that are discussed next.

Chemical Requirements

The most useful chemical requirements that are contained in many standard specifications of the world, such as the Canadian CAN 3-A 23.5 and the ASTM C 618, are those requiring a maximum limit of 10 percent on ignition loss and 3 percent on free moisture. The object of these requirements is to insure that the pozzolan is in a dry and suitably-calcined state before use.

The most controversial chemical requirement in ASTM C 618 is the one prescribing that the sum of the three principal oxides (i.e., SiO_2 + Al_2O_3 + Fe_2O_3) must be more than 70 percent. When present in a non-crystalline (glassy) or poorly crystalline state, these constituents participate in pozzolanic activilty reactions. The ASTM C 618 minimum requirement on the sum of SiO_2, Al_2O_3, and Fe_2O_3, assumes that in pozzolans these oxides are always present in a reactive form, which is seldom correct. Most natural pozzolans contain substantial amounts of quartz and feldspar, which are highly

crystalline and non-reactive to lime. Commenting on the ASTM C 618 requirement on the content of $SiO_2 + Al_2O_3 + Fe_2O_3$, Lea (1) says:

> These overall composition requirements do not appear in European specifications and indeed the U.S. minimum requirements comes close to rejecting some of the Roman pozzolans. It cannot be said that such overall limitations on composition have much practical value, and they can be unnecessarily restrictive.

Attempts have often been made to determine the content of active constituents in a pozzolan by acid and alkali leaching, and much of the work is summarized by Lea. Extraction with hot or cold hydrochloric acid or nitric acid, or with alkali hydroxide and carbonate solutions have failed to reveal any relationship between the acid or alkali soluble material and the strength contribution potential of a pozzolan in a portland cement mortar or concrete.

Some specifications require determination of the pozzolanic activity from chemical tests on the lime fixation capacity of the pozzolan. Only in some cases a close relationship has been found between the lime fixation capacity of the pozzolan and the strength of a standard mortar made with the portland-pozzolan cement. Many researchers including Massazza (21), and Takemoto and Uchikawa (14) have concluded that there is no relationship in the data from the two tests. Since the strength of a mortar is directly attributable to the microstructure of the hydrated cement paste present (i.e., the intrinsic strength of the hydration product and the pore size distribution of the system), Regourd et al. (22) point out that the microstructure in the two cases may not be the same.

Physical Requirements

From the standpoint of a simple method for quality control on pozolanic activity a test and a specification for the maximum permissible amount of coarse particles in a pozzolan is very useful. ASTM C 618 limits the 325 mesh sieve residue (> 45 μm) to 34 percent; some others prefer a lower limit, such as the Indian Standard IS-1344 which permits a maximum of 12 percent particles only above 45 μm.

Particle size is one of the parameters controlling the pozzolanic activity; others are the composition and amount of reactive constituents such as glass, which is difficult to determine. Most standard specifications, therefore, require a direct test for the pozzolanic activity and a minimum value of the activity index. Typically, this test involves the determination of compressive strength of a test mortar containing either a lime-pozzolan or a portland cement-pozzolan mixture of specified proportions and cured under given conditions. Due to the variable quality of lime and its effect on the test results, many investigators do not favor the lime-pozzolan test.

In the ASTM C 311 pozzolanic activity test with portland cement, the test mortar contains 35 percent cement replacement (by volume) by the pozzolan. The water/cement ratio of the test mortar is not fixed; it is variable and is determined by a standard consistency test. This is an objectionable feature of the ASTM C 311 pozzolanic activity test method. Strength of a cement depends on the initial porosity (i.e., water/cement ratio), and the degree of pore space filled by the hydration products. If different water/cement ratios have been used for testing the pozzolanic activity of two pozzolans, then the strength data corresponding to a given degree of hydration would not give a true index of their pozzolanic activity because the strength is also affected by the initial porosity.

Due to their microporous character and high surface area, most natural pozzolans tend to increase the water requirement in the standard consistency test. Most standard specifications contain an arbitrary limit on the maximum water requirement. Such arbitrary limits can be unduly restrictives because an excessive water requirement may be corrected by the application of a water-reducing agent (23).

The ASTM C 618 also contains a specification for soundness which is based on a test method involving the exposure of the portland cement-pozzolan paste to high temperature and pressure conditions in an autoclave. This method was originally developed for the evaluation of soundness of portland cement containing undesirably large amounts of crystalline MgO or CaO. Natural pozolans contain neither of the expansive oxides, and therefore have no difficulty in complying with the requirements of the soundness test and the specification. It is generally agreed that the soundness test and specification are of no value and should be deleted from the standards.

PROPERTIES OF CONCRETE CONTAINING NATURAL POZZOLAN

Modifications in properties of portland cement concrete as a result of addition of a pozzolan include slower rate of setting and hardening, higher ultimate strength, lower heat of hydration, and better performance in acidic environments. Clearly, these technical advantages from the use of pozzolans in concrete are not limited to natural pozzolans; they can also be obtained from the use of industrial byproducts such as fly ash. However, only natural pozzolans fall within the scope of this paper.

Setting Time

The addition of a natural pozzolan to portland cement results in set retardation due partly to the dilution effect (i.e., the dilution of the most active ingredient, which is portland cement) and partly to the increased water requirement for making a paste of normal consistency. For instance, Nicolaidis (24) reported that, compared to the neat portland cement both the initial and final setting times of a blended portland cement containing 20 percent Santorin Earth were increased by 20 minutes. The water requirements to produce a paste of normal consistency were 24.5% and 26.5% for the portland cement and the blended portland cement, respectively.

Bleeding

Many investigators have observed that with blended portland cements containing pozzolans, the rate of bleeding is reduced considerably. For example, using the ASTM Method C 243-55, Nicolaidis (24) found in his investigation bleeding rates of 127×10^{-6} and 84×10^{-6} cm^3/cm^2 sec. for the portland cement and the portland-pozzolan cement (containing 20 percent Santorin Earth), respectively. Even more impressive a reduction in bleeding was obtained by Davis and Klein (16) by using finely ground diatomite from Lompoc (California) in a lean concrete mixture. The 1-hr. bleeding in the reference concrete (without the diatomite) amounted to 22 percent of total water present. When 11% of the cement by weight was replaced with the diatomite, the bleed water was only 2 percent of the total water.

The reduction in bleeding is due partly to the interference provided by the finely pulverized particles of the pozzolan to the water flow channels in a freshly consolidated concrete mixture and partly to the microporous

character of the pozzolanic materials. It is believed now that the control of internal bleeding in concrete plays an important role in determining the strength of the transition zone between aggregate and cement paste and therefore the mechanical properties of concrete (25).

It should be noted that the water retention characteristics of natural pozzolans, such as volcanic ashes and calcined clays distinguishes them from byproduct pozzolans such as fly ash. The incorporation of the former tends to increase the water requirement of concrete but of the latter has generally a water-reducing effect. The higher water/cement ratio of a concrete mixture containing a natural pozzolan may not necessarily impair the strength because a part of the mixing water will be adsorbed by the pozzolan and thus will not cause a corresponding increase in the porosity of the hardened concrete. According to Nicolaidis (23), this adsorbed water would later be available for the pozzolanic reaction.

Heat of Hydration

Using a natural pozzolan from Italy, Massazza and Costa (13) showed that the addition of the pozzolan to a portland cement clearly reduced the heat of hydration (Fig. 6), however this reduction was not directly proportional to the amount of cement replaced. It was smaller because of the slow heat evolution due to the pozzolanic reaction. For example, at the 20 percent level of cement replacement, the 90-day heat of hydration of the portland cement was reduced from 94 to 85 cal/g. and the 28-day heat of hydration was reduced from 85 to 76 cal/g. Similarly, with 20 percent cement replacement by Santorini Earth in the case of a Greek portland cement, Nicolaidis (24) found that the 7-day heat of hydration was reduced by 9 cal/g.

The ability of the pozzolanic materials to reduce the heat of hydration in portland-pozzolan cements is widely exploited in the construction of mass concrete structures, where the risk of thermal cracking can be a major problem. For this purpose, as described earlier, natural pozzolans were used first in in the United States in 1910 to 1912 for the construction of Los Angeles Aqueduct and later in the construction of San Francisco Bay Bridge, Golden Gate Bridge, Friant Dam, Bonneville Dam, Davis Dam, Glen Canyon Dam, Flaming Gorge Dam, Wanapum Dam, and John Day dam (9).

Strength

Although the pozzolanic reactions in a portland-pozzolan cement paste begin as soon as alkalies and calcium ions are released during the hydration of portland cement, most of the pozzolanic activity and therefore the strength development associated with it seems to occur after 7 days of hydration. Typical results from an investigation on the effect of curing time on the compressive strength of ASTM C 109 mortars made with portland-pozzolan cements containing 10, 20, or 30 percent Santorin Earth, are presented in Figs. 7 and 8.

From the compressive strength data for 1, 3, 7, and 28 days (Fig. 7), it is evident that up to 7 days the strength was approximately proportional to the amount of portland cement present in the blended cement. This shows that in 7 days of hydration the pozzolanic reaction had not progressed far enough to influence the strength. At 28 days, however, the strength of the cement containing 10 percent pozzolan was slightly higher than the reference portland cement; the cements containing 20 percent and 30 percent pozzolan showed 7% and 18% lower strengths than the control, respectively. It was concluded from

the data in Fig. 7, that during the 7 to 28 days hydration period the beneficial effect on strength due to the pozzolanic reaction was not considerable.

The strength data for 28- and 90-day, and 1-year in Fig. 8 shows that at 90-day the strength of both 10 percent- and 20 percent-Santorin Earth cements was about 10% greater than the reference portland cement. The 1-year strength of the 30 percent pozzolan cement was similar to the reference portland cement whereas the other two pozzolan cements showed higher strength than the control. In Fig. 9 similar results on the effect of substituting portland cement with an Italian natural pozzolan are reported by Massazza and Costa (13). The authors confirm the slow reaction between lime and pozzolan and conclude that at early ages, the cements containing pozzolans show lower strength than the reference portland cement; however, the ultimate strength can be higher depending on the quality and quantity of the pozzolan used. It seems that an excess of pozzolan, viz. more than 40 percent by weight in the blended cement, should be avoided when a substantial reduction in the mechanical strength of the product cannot be tolerated especially at early ages and under cold weather conditions.

Durability to Sulfate Attack

The sulfate attack in concrete generally involves expansion, cracking and loss of mechanical strength due to the formation of ettringite and gypsum. These minerals are formed as a result of interaction between a sulfate water and cement hydration products, such as the monolsulfate hydrate ($C_4A\bar{S}H_{18}$) and calcium hydroxide (CH). Sea water and ground waters from alkaline soils are the common sources of sulfate in natural waters.

It is well known that the use of natural pozzolans in the form of cementitious lime-pozzolan mixtures or portland cement-pozzolan mixtures has a beneficial effect on the durability of concrete exposed to sulfate water. This is because the pozzolanic reactions not only reduce the permeability of concrete but also result in the formation of a sulfate resisting product (i.e., less calcium hydroxide present in the hydrated cement paste, and a C-S-H with lower CaO/SiO_2 ratio). The results from numerous laboratory investigations including those discussed below seem to confirm that the addition of a natural pozzolan enhances the sulfate resistance of portland cement.

Massazza and Costa (13) reported the effect of substituting portland cement with 10, 20, or 30 percent of an Italian pozzolan on the expansion of 1:3 mortar prisms stored for more than 5 years in a 1% $MgSO_4$ solution (Fig. 10). With the mortars containing 30 or 40 percent cement replacement by the pozzolan, the expansion was considerably reduced. The authors attributed the results to the reduced content of calcium hydroxide and higher impermeability. According to them, the free calcium in hydrated pozzolan cements would not only be present in a lower amount but would be surrounded by impermeable C-S-H gel. These conditions are unfavorable to the formation of ettringite, which is generally considered to be the agent causing expansion and cracking.

In another study the effect of substituting Santorin Earth, 10, 20, or 30 percent by weight on the sulfate resistance of a Type 1 portland cement was investigated by two methods (12). In the first method, mortar prisms made with a sand/cement ratio of 2, and a water/cement ratio of 0.6, were moist-cured at normal temperature for 28 days and then immersed in 10% Na_2SO_4 solution. The solution was changed once every week and the expansion date for prisms were measured at various intervals up to 26 weeks (Table 4). Again, for the reasons given above, it may be observed from the expansion data that

the sulfate attack was considerably less severe on the mortars made with 20 or 30% pozzolan cements.

The second test for sulfate resistance of the blended portland cements containing Santorin Earth involved an accelerated method (26). According to this test, the criterion for sulfate resistance is the relative loss in compressive strength when specimens of neat cement paste are immersed in a 4% Na_2SO_4 solution, which is maintained at a constant pH and sulfate concentration. Before the sulfate immersion the specimens were subjected to accelerated curing at 50°C for 7 days. In this test the cements showing 25% or higher strength loss in 28 days of sulfate exposure are presumed to perform unsatisfactorily. Again, the test data shown in Table 5 confirmed the conclusion from the first test that cements containing 20 or 30 percent Santorin Earth were resistant to sulfate attack. Whereas the reference portland cement and the cement containing 10 percent Santorin Earth did not lose more than 20% strength as a result of sulfate immersion, the cements containing 20 or 30 percent Santorin Earth did not lose more than 20% strength.

Studies by Davis et al. (27) regarding the influence of various natural pozzolans from California on the resistance of the cement to this action of a sodium sulfate solution showed why some pozzolan types are useful in combating the sulfate attack whereas the others are not. Blended portland cements containing crystalline silicas, granite and quartz reduced the sulfate resistance of the cement, however the cements containing reactive silica, such as monterey shale, diatomaceous earth, and pumicite, improved the resistance of the cement to sulfate attack. This confirms the earlier analysis that only those pozzolanic materials that are capable of entering into pozzolanic

reaction with lime can be relied upon to offer the technical advantages associated with the use of a pozzolan in concrete.

Resistance to Alkali-Silica Expansion

The chemical interaction of certain siliceous mineral constituents of aggregate with the alkalies in portland cement is known to cause expansion and cracking of concrete. The commonly practiced method of reducing the risk of such expansion is the use of a low-alkali cement. Alternatively, where possible, the reactive aggregate source is replaced by a non-reactive source. When the use of a high-alkali portland cement (> 0.6% Na_2O equivalent) in combination with an aggregate containing an alkali-reactive constituents seems unavoidable, the expansion phenomenon may be controlled by incorporating into the concrete mixture a pozzolanic material that has proven in laboratory tests to be effective in reducing the alkali-aggregate expansion.

The mechanisms by which the alkali-silica reaction in concrete is able to cause expansion and the use of a pozzolanic material reduces the expansion, are not fully understood. Some researchers assume that the expansion and cracking are caused by the osmotic pressure when the alkali-silicate gels imbibe large amounts of water. Thus it is suggested that depending upon the particle size, reactivity, and the amount of pozzolan added, the alkali-silica gel may be evenly distributed throughout the concrete with the result that there is no opportunity for the formation of a large mass of gel that would cause sufficient localized osmotic pressure to rupture the concrete (28,29). Others believe that in the presence of pozzolans, instead of alkali-silica gels the alkali-lime-silicates of low alkali to silica ratio, which have only slight solubility, are formed.

Regardless of the mechanism by which the expansion associated with the alkali-silica reaction, and not the alkali-silica reaction itself, is

controlled by the incorporation of a pozzolan in concrete, it has been observed by many investigators that natural pozzolans are found to be more efficient for this purpose than byproduct pozzolanic materials. For instance, Pepper and Mather (30) found that the percentage by solid volume of the pozzolan needed to replace portland cement for adequate reduction of expansion (as required to meet the requirements of the ASTM C 441) varied from 20 percent with diatomite, 20 to 30 percent with calcined shale, and 40 to 50 percent with fly ash.

All natural pozzolans are not equally effective in combating alkali-silica expansion. Pepper and Mather (30) reported that in the case of a volcanic glass cement replacement on the order of 30 to 35 percent was needed to meet the requirements of the ASTM C 441. Similarly, using an accelerated test procedure (30), the results of an investigation showed (Fig. 1) that portland cements (1.0% equiv. Na_2O) containing 20 or 30 percent Santorin Earth were quite satisfactory with regard to control of the alkali-silica expansion. It may be pointed out here that many natural pozzolans themselves contain a high alkali content. For instance, the chemical analysis of the Santorin Earth (Table 1) shows 3.9% Na_2O and 2.6% for K_2O (5.6% Na_2O equiv.). It seems that under normal conditions in concrete the alkali ions, bound in the framework-type crystal structure of feldspar or mica, are not released and therefore do not play any deleterious role in alkali-silica expansion.

Durability to Frost Action

Incorporation of natural pozzolans does not impair the freeze-thaw durability of concrete provided the concrete has been adequately protected by air entrainment. Very finely ground pozzolans tend to reduce the amount of entrained air in a concrete mixture and therefore may require a higher than

normal dosage of the air-entraining admixtures to obtain a given amount of entrained air.

Drying Shrinkage and Creep

The drying shrinkage of products made with portland-pozzolan cements is generally higher than the corresponding product containing portland cement alone. This is to be expected because the drying shrinkage of a hydrated cement paste is generally attributable to the content of C-S-H, which would be relatively more in the case of portland-pozzolan cements. However, many researchers have observed that the cracking tendency due to drying shrinkage in concretes containing pozzolans is less than the corresponding concretes without pozzolans.

There are probably two explanations for the phenomenon why the incidence of drying shrinkage cracking in portland-pozzolan cement products is not as high as expected. First, it seems that the restraining effect of aggregate on the shrinkage of the cement paste in mortar or concrete plays an important part in determining the total amount of the shrinkage. In a 90-d shrinkage test involving mortar prisms by Massazza and Costa (13), it was found that compared to 890 μm/m for ordinary portland cement, the drying shrinkage of the cement containing an Italian pozzolan was only 943 μm/m. In another study using concrete prisms and an 80-weeks drying period, it was found that compared to the reference portland cement the drying shrinkages of concretes made with blended cements containing 10, 20, or 30 percent Santorin Earth were not significantly different (Fig. 12).

The second explanation for relatively less cracking in portland-pozzolan cement products lies probably in the stronger transition zone between the aggregate and cement paste, compared to a corresponding concrete (with similar

water/cement ratio) without the pozzolan. Therefore, at a given ratio of water to the cementitious material, the flexural and tensile strengths of portland-pozzolan cement concrete tend to be higher than the pozzolan cement concrete. This increases the tensile strain capacity and hence the crack resistance of the former under given shrinkage conditions.

Creep is influenced by the amount of C-S-H as well as by the rate of hardening of concrete. Concretes containing pozzolans, therefore, tend to show somewhat higher creep than the corresponding portland cement concretes.

THE USE OF NATURAL POZZOLANS IN THE FUTURE

When properly employed as an ingredient of portland-pozzolan cements or as admixtures to portland cement concrete, pozzolans can improve the performance of both fresh and hardened concrete. In fact, some of the technical advantages made possible by the use of pozzolans in concrete are not attainable when ordinary portland cement is used alone. The advantages include improvement in workability, reduction in heat of hydration, increase in watertightness, and enhanced resistance to sulfate attack and alkali-aggregate expansion. In addition, the use of pozzolans in concrete is frequently cost-effective and energy saving.

Industrial byproducts such as fly ash and condensed silica fume are finding increasing use as pozzolans, because they are plentiful in many parts of the world and unlike natural pozzolans they usually do not require any pulverization or thermal treatment before use. However in several countries, viz., China, Greece, Italy, India, Mexico, millions of tons of natural pozzolans are still being used for making blended portland cements. For reasons of economy and energy-saving, their use is expected to continue or even increase in the future.

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Table 1

Typical Chemical Analyses of Some Natural Pozzolans, %

Pozzolan	SiO_2	$A\ell_2O_3$	Fe_2O_3	CaO	MgO	Alkalies	Ignition Loss	Reference
Santorin Earth	65.1	14.5	5.5	3.0	1.1	6.5	3.5	11
Rheinish Trass	53.0	16.0	6.0	7.0	3.0	6.0	-	4
Phonolite	55.7	20.2	2.8	4.2	1.1	10.8	3.6	5
Roman Tuff	44.7	18.9	10.1	10.3	4.4	6.7	4.4	12
Napolitan Glass	54.5	18.3	4.6	7.4	1.0	11.0	3.1	12
Opaline Shale	65.4	10.1	4.2	4.6	2.7	1.4	6.3	14
Diatomite	86.0	2.3	1.8	-	0.6	0.4	5.2	14
Rhyolite Pumicite	65.7	15.9	2.5	3.4	1.3	6.9	3.4	14
Jalisco Pumice	68.7	14.8	2.3	-	0.5	9.3	5.6	10

Table 2

Mineralogical Analysis of Some Natural Pozzolan

Pozzolan	Estimated noncrystalline matter, %	Major crystalline minerals	Reference
Santorin Earth	65-75	quartz, anorthite, labradorite	11,23
Rheinisch Trass	50-60	quartz, feldspar, analcine	15
Phonolite	-	orthoclase, albite, pyroxene, calcite	5
Roman tuff	-	herschelite, chabazite, phillipsite	1
Napolitan glass	50-70	quartz, feldspar	19
Jalisco pumice	90	sanidine	10

Table 3*

Relative Depth of Penetration of Water
into Hydrated Cement Pastes, mm

Hydration Age	Portland Cement	10 Percent Santorin Earth	20 Percent Santorin Earth	30 Percent Santorin Earth
28 days	26	24	25	25
90 days	25	23	23	22
1 year	25	23	18	15

*Reference 11 (P. K. Mehta)

Table 4*

Expansion of Mortar Prisms in Sulfate Solution, %

Cement Type	4 Weeks	8 Weeks	12 Weeks	26 Weeks
Portland Cement	0.004	0.034	0.212	0.520
10% Santorin Earth	0.006	0.018	0.071	0.285
20% Santorin Earth	0.007	0.010	0.048	0.072
30% Santorin Earth	0.006	0.008	0.027	0.050

*Reference 11 (P. K. Mehta)

Table 5*

Compressive Strength Loss of Cement Paste Cylinders
in Sulfate Solution Held at Constant pH

Cement Type	Strength Before Immersion, MPa	Strength After 28 Days Immersion, MPa	Strength Loss
Portland Cement	18.0	6.1	65%
10% Santorin Earth	18.5	9.5	49%
20% Santorin Earth	16.1	12.9	20%
30% Santorin Earth	15.2	12.8	16%

*Reference 11 (P. K. Mehta)